PAPER

Dual channel chromo/fluorogenic chemosensors for cyanide and fluoride ions – an example of *in situ* acid catalysis of the Strecker reaction for cyanide ion chemodosimetry†

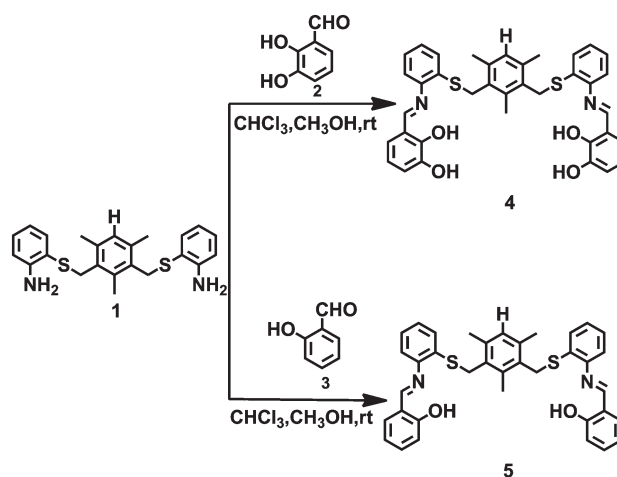Sanyog Sharma, Maninder Singh Hundal* and Geeta Hundal*

Two mesitylene based probes, having catechol/phenol units in conjunction to the Schiff base have been synthesized. The probe with a catechol unit can be used to sense and discriminate between F⁻ and CN⁻ through different colorimetric and fluorimetric responses using DMSO as solvent. However in DMSO : water (2 : 1) solution it responds selectively to CN⁻ ion. The probe with a phenol unit is highly selective and sensitive for CN⁻ and can be used for naked eye, semiquantitative sensing of CN⁻ ion in DMSO : water (2 : 1) solution. The chemodosimetry has been attributed to the acid catalyzed Strecker's reaction of an imine bond and is being reported for the first time in a Schiff's base.

Introduction

The importance of anions in biological, environmental and chemical processes has given impetus to the development of anion sensing receptors.[1,2] Among various anions, fluoride and cyanide have been extensively studied. The fluoride ion is undoubtedly important[3] in health care but its increasing use in the synthesis of materials and biological catalysis[4] has led to its unwanted release, notwithstanding its 0.2 μM limit in drinking water. Similarly, the continued use of cyanide ion in various industrial processes[5] causes its inevitable release in the environment though 2 μM is its maximum allowed concentration in drinking water and 20 μM is considered as its lethal level.[6] Consequently there is always a need to develop sensors to monitor these anions, and even more so for having a multi-analyte sensing chemosensor catering to more than one ion with distinctive and selective responses. As most of the chemosensors for CN⁻ ion suffer from unsolicited interference from other ions, in particular the F⁻ ion, therefore the selectivity is a paramount issue.[7] While there are fewer known chemodosimeters[8] for F⁻ ions, this sensing approach has been quite successfully used in the case of CN⁻ ions owing to its strong nucleophilicity.[9] Despite all these reports the nucleophilic

addition of CN⁻ to a Schiff base's imine bond has scarcely been studied. The closest examples to this system are the two chemodosimeters using salicylaldehyde hydrazone functionality[10] where addition of cyanide to the imine bond of the hydrazones has been suggested.

We have synthesized two mesitylene based dipodal Schiff base systems incorporating catechol (**4**) and phenol (**5**) units as the end groups (Scheme 1) and exploited the anion recognizing ability of the –OH group in conjunction with the imine group. In DMSO, **4** has been found to act as a naked eye chromogenic and ratiometric fluorogenic sensor for F⁻ ion. This compound also behaves as a dual channel chromogenic

Department of Chemistry, Guru Nanak Dev University, Amritsar-143005, Punjab, India. E-mail: geetahundal@yahoo.com, hundal_chem@yahoo.com

†Electronic supplementary information (ESI) available: General experimental section, characterization of sensors by NMR, IR and mass spectroscopy, changes in visible color and under UV lamp, absorption spectra, titration study of (**4**) and (**5**) and characterization of chemodosimeter (**6**). CCDC 898519. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob27096j
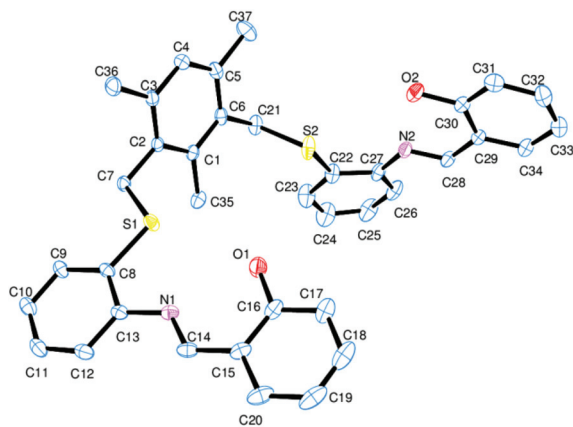

Scheme 1 Synthesis of sensors.

Fig. 1 ORTEP diagram for (**5**) showing the labeling scheme. Hydrogens and solvent CCl_4 have been omitted for clarity.

Fig. 2 Changes in the UV-vis spectrum of **4** in DMSO (10 μM) on the addition of various anions (100 μM).

sensor or a chemodosimeter, depending on the concentration of CN^- ion in DMSO. In water, however it behaves as a highly selective sensor for CN^- ion only. Probe (**5**) acts as an exclusive, naked-eye, concentration dependent chromo-fluorogenic sensor and a chemodosimeter for cyanide ion. Such a chemodosimeter response, to the best of our knowledge is being studied for the first time in a Schiff base. It is attributed to the *in situ* acid catalysis of the Strecker reaction,[11] giving addition of CN^- anion to the imine bond.

Results and discussion

The sensors (**4**) and (**5**) were synthesized as shown in Scheme 1, by a Schiff base condensation reaction of reactant amine[12] **1** with **2** or **3**, respectively in a chloroform–methanol mixture in the presence of $Zn(ClO_4)_2$ as catalyst. These compounds have been characterized by elemental analyses, IR, ^1H, ^{13}C NMR, mass, UV-vis absorption spectroscopy and X-ray analysis (Fig. S1–S10†).

X-ray crystal structure of (5)

The crystal structure determination of (**5**) reveals (Fig. 1) that a solvent molecule of CCl_4 gets incorporated during crystallization. The structure shows that the dipodal molecule has an approximate 'U' shaped conformation with the central anchor phenyl ring forming the base. There are strong intramolecular H-bonding interactions between the OH groups and imine nitrogens as well as the S atoms which are supporting this conformation. The details of the characterization data as well as the crystal structure are given in the ESI (Fig. S11–S13†).

Colorimetric and chromogenic spectral response of (4)

The anion binding ability of receptor (**4**) (10 μM) was determined by the changes in its absorption spectra measured upon addition of various tetrabutylammonium anions, TBAX (where X = F^-, Cl^-, Br^-, I^-, NO_3^-, CN^-, ClO_4^-, AcO^-, HSO_4^- and $H_2PO_4^-$) in DMSO (100 μM) (Fig. 2). Upon addition of F^- and CN^-, significant changes in the spectra were observed.
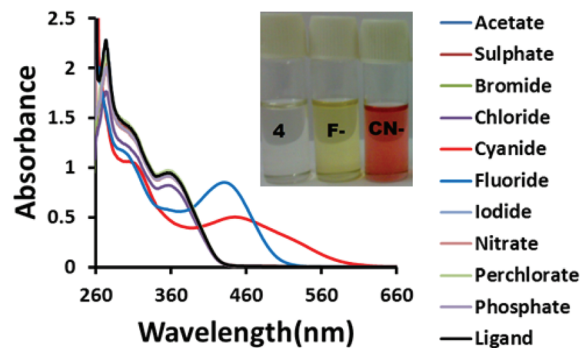
With F^-, the intraligand charge transfer (ICT) band[13d,14] at λ_{max} 355 nm disappears and a new peak appears at λ_{max} 431 nm (ε_{max} 7.3 × 10^4 M^{-1} cm^{-1}) with a concomitant color change from pale yellow to bright yellow. But in case of CN^-, a new absorption peak appears at λ_{max} 445 nm with a lower absorption (ε_{max} 5.0 × 10^4 M^{-1} cm^{-1}) which then shifts to 469 nm (ε = 5.5 × 10^4 M^{-1} cm^{-1}) and then tails off up to 600 nm. The bathochromic shift increases with time (Fig. S14†) and/or with further addition of TBACN. The saturation causes the appearance of a new broad band at 500 nm (ε = 6.3 × 10^4 M^{-1} cm^{-1}). These spectral changes are accompanied with visual color changes from pale yellow to bright yellow to reddish orange. There are no visual or spectroscopic changes with Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, AcO^-, HSO_4^- and $H_2PO_4^-$ ions.

As (**4**) responded to both F^- and CN^- ions to have a better insight into the recognition phenomenon UV-vis titrations were performed. On addition of aliquots of TBAF, to a solution of (**4**) in DMSO (Fig. S15†), a significant change was observed even with 1 μM of anion, so the detection limit[15] of fluoride has to be less than 1.5 μM. The reaction of (**4**) with TBAF gives a binding constant, K = 4.68 × 10^3 M^{-1} and shows a 1 : 1 stoichiometry (Fig. S16†). This reaction is completely reversible on addition of water to it suggesting that deprotonation is involved in the colorimetric response. On the other hand, gradual addition of CN^- anion to (**4**) leads to a band at 445 nm at a lower concentration (<37 μM), but at a higher concentration (from 37 to 700 μM) the latter shifts to a longer wavelength at $\lambda_{max.}$ 496 nm (Fig. S17†). The stoichiometry of the reaction is 1 : 2 as found by the Job's plot and a binding constant K = 7.27 × 10^3 M^{-1} (Fig. S18†). The changes are fully reversible at lower concentrations of the anion but irreversible at the higher concentrations *i.e.* the red color once attained does not disappear not even on addition of water. The detection limit of cyanide in a solution of (**4**) in DMSO was found to be less than 3 μM (Fig. S17†). Addition of TBAOH to (**4**) causes changes similar to TBAF (Fig. S19†) and no bands at longer wavelength were found which means that the sensing involves deprotonation of the catechol moieties in the presence of more basic F^- ion in DMSO. In the case of CN^- ion which is a weaker base but a stronger nucleophile, it is proposed that
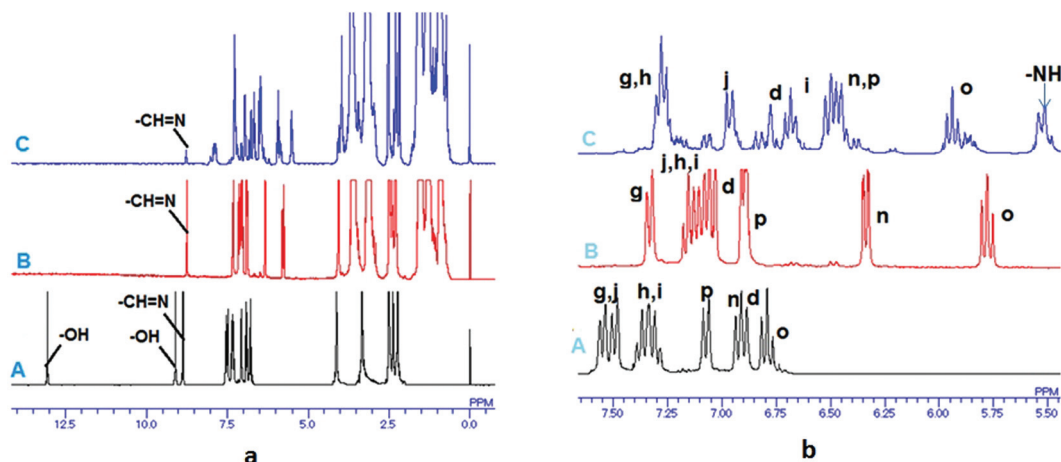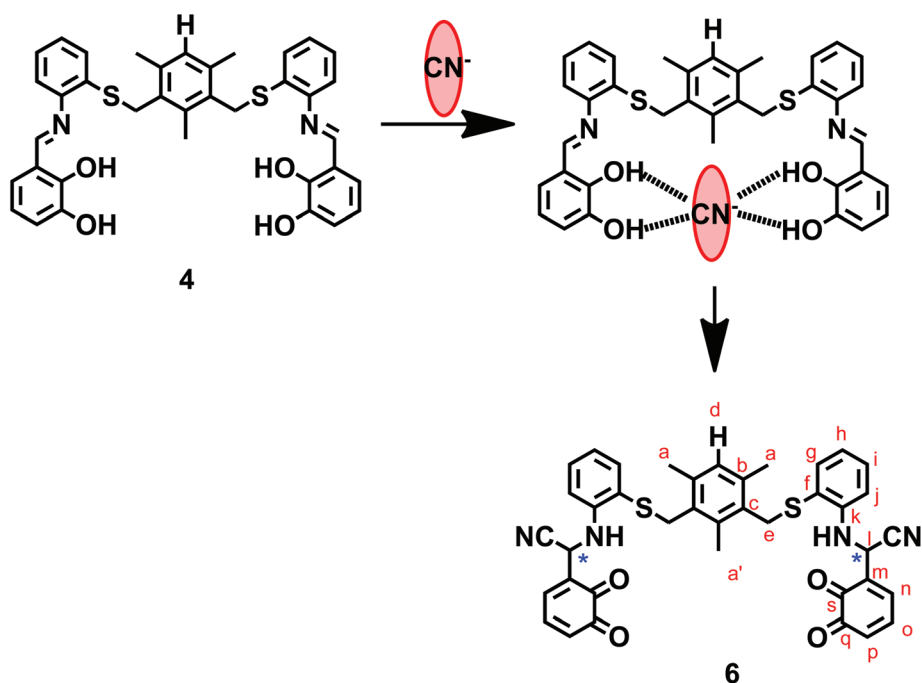
This journal is © The Royal Society of Chemistry 2013

Org. Biomol. Chem., 2013, **11**, 654–661 | **655**

Fig. 3 (a) Full (b) partial ^{1}H NMR of (**4**) in DMSO-d$_6$ (5 mM) showing changes on addition of F$^-$ and CN$^-$ anions. (A) Sensor alone (B) with TBAF (50 mM) (C) with TBACN (50 mM) [labels used in the diagram are shown in ESI, Scheme S1†].

Scheme 2 Proposed reaction mechanism for chemodosimeter formation (**6**).

deprotonation further leads to nucleophilic attack at the –C=N bond. Thus (**4**) acts as a visual chromogenic chemosensor for F$^-$ ion and a unique double channel operating sensor which behaves as a chemosensor for CN$^-$ at a concentration ~40 μM (4 equivalents) and a 'naked eye', concentration or time dependent, chemodosimeter above it. Moreover the visual color changes within 2–3 minutes give different responses to F$^-$ and CN$^-$ anions and thus may be used for their discrimination.

^{1}H and ^{13}C NMR titration experiments of (4)

The above proposed chemodosimeter is based upon the ^{1}H and ^{13}C NMR changes found on addition of 10 equivalents

of TBAF and TBACN to a solution of (**4**) in DMSO-d$_6$. Fig. 3a shows the changes found in the aromatic region in the ^{1}H NMR for (**4**) on their addition. In both cases the –OH signals have disappeared and the spectra show the expected up field in almost all the signals. Most significant, however is the disappearance of the imine signal at δ 8.875 and appearance of a doublet at δ 5.526 in the case of CN$^-$ but not in the case of F$^-$ ion (Fig. 3b). These changes have been attributed to the occurrence of a Strecker's reaction[11] by nucleophilic addition of CN$^-$ ion on the imine bond resulting in the formation of a nitrile (**6**) (Scheme 2). It is well known that the poor reactivity of the imine bond requires activation for satisfactory efficiency in the Strecker reaction and hence is
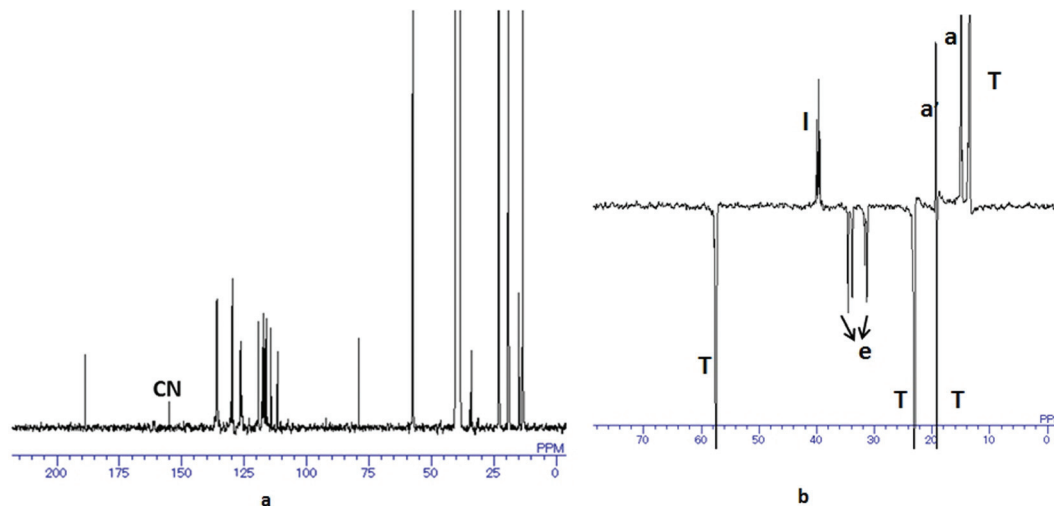
Fig. 4 Showing the (a) ^{13}C NMR (b) partial DEPT-135 of (**4**) in DMSO-d_6 with TBACN in it, T represents signals due to TBA.

generally activated by a Brønsted or Lewis acid by forming iminium ions[16] in the case of those imine groups which are not substituted by an activating group. In the present case, the potential H-bonding pocket defined by four catecholic –OH protons which have the potential to bind anions in a chelate mode, tends to bring the cyanide to their vicinity. Deprotonation of the –OH groups results in generation of H^+ ions which activate the imine group and a nucleophilic addition reaction of CN^- occurs forming a nitrile.

A dependence of the change on concentration of the anion suggests that deprotonation is just one step in a multi-step process. The doublet at δ 5.526 is assigned to the amine proton and the corresponding signal due to imine proton disappears. The signal due to the proton attached to the chiral C is overlapped by the signals due to tetrabutylammonium cation. As the product (**6**) obtained is a mixture of diastereomers with a possible diastereomeric excess of one enantiomeric pair, each signal in the NMR is accompanied by another signal of much lesser intensity. The formation of (**6**) is well supported by the changes in the ^{13}C NMR of the addition product (Fig. 4a) where the signal at δ 162.9 ppm due to imine carbon is absent but a signal appears at δ 155 ppm corresponding to the carbon of the added CN group (absent in DEPT-135) on the positive side (Fig. 4b).

The signal due to the chiral α-C (Scheme 2) is again overlapped by the signals of DMSO in the ^{13}C NMR spectrum but is clearly visible at δ 39.7 ppm in the DEPT on the positive side (Fig. 4b). The electrospray ionization mass spectrum (Fig. S20†) of this solution in DMSO shows a base peak at 786.85 which corresponds to an adduct of DMSO and Na with $[(M + 1)]^+$ ion (calculated 786.15) which clearly proves the formation of (**6**) during the sensing experiment. Based on the above evidence it may be concluded that (**4**) behaves as a chemodosimeter for CN^- induced deprotonation. At low concentrations of the anion the nitrogen of the imine group is not protonated and the imine group is not activated for nucleophilic attack by the CN^- ion therefore (**4**) behaves as a

chromogenic sensor only. On the other hand due to the high basicity of the $[HF_2]^-$ ion which is produced in the presence of F^- ion and is recognizable by the tell-tale triplet at 16.1 (Fig. S21†) it acts as a chromogenic sensor for it.

Fluorogenic spectral response of (4)

The fluorescence spectral changes of (**4**) with various anions (Fig. 5) make it a highly selective ratiometric fluorogenic sensor for F^- ion with very small interference only from CN^- ion which vanishes at a higher concentration of analyte. The ligand does not have any fluorescence when excited at 350 nm but on the addition of TBAF an emission band appears at 560 nm with high intensity. This gives a fluorescent green color under a UV lamp (Fig. S22a†) and the emission has been attributed to the well-known ESIPT phenomenon in such Schiff bases where the steady state emission is dominated by cis-keto tautomer formed after photoinduced proton transfer.[17]

Colorimetric, UV-vis and fluorogenic spectral response of (5)

Among ten anions tested in DMSO, (**5**) responded only to the CN^- ion as is evident from the absorption (Fig. 6) and emission bands (Fig. 7) resulting in a color change from almost colorless to yellow which moves towards reddish with time (Fig. S23†). From the absorption spectra at 10 equiv. of the added anion the band at λ_{max} 350 nm has completely vanished and a new, very broad band starts appearing at 465 nm (Fig. S24†). The detection limit of cyanide in solution of (**5**) was found to be less 3 μM. A comparison with the –OH ion (Fig. S25†) shows that the channel working for sensing is similar to (**4**) i.e. H-bonding at low concentration and due to deprotonation and chemodosimetry, at a higher concentration (with a 1 : 2 stoichiometry and binding constant of 3.53 × 10^2 M^{-1} (Fig. S26†). The lesser sensitivity of (**5**) towards chemodosimetry is expected due to phenol being less acidic than catechol and has one proton only, deprotonation and subsequent activation of the imine nitrogen is achieved at a
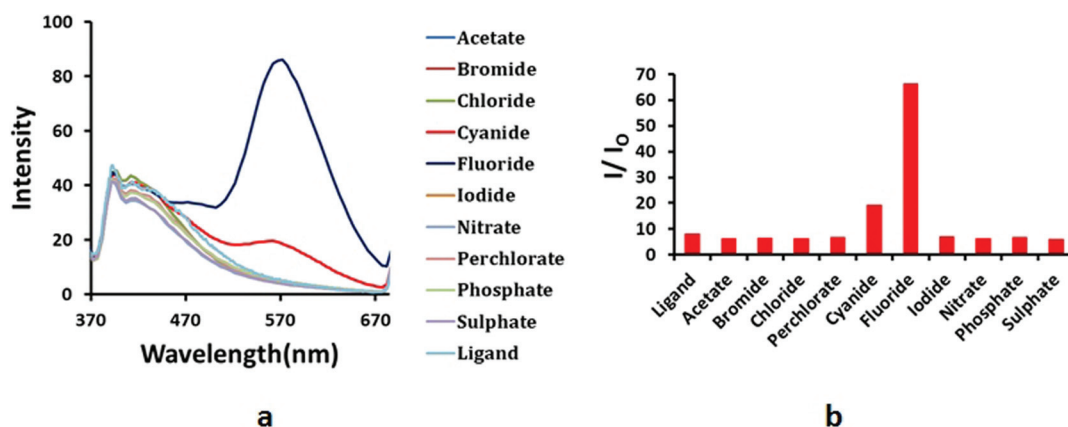
This journal is © The Royal Society of Chemistry 2013

Org. Biomol. Chem., 2013, **11**, 654–661 | **657**

Fig. 5 Showing (a) changes in the fluorescence intensity b) fluorescence ratio [I/I_o] of sensor (**4**) (5 μM) at λ_{max} 560 nm upon addition of various anions (50 μM) with excitation at 350 nm in DMSO. I_o and I are the intensities in the absence and presence of anions respectively.
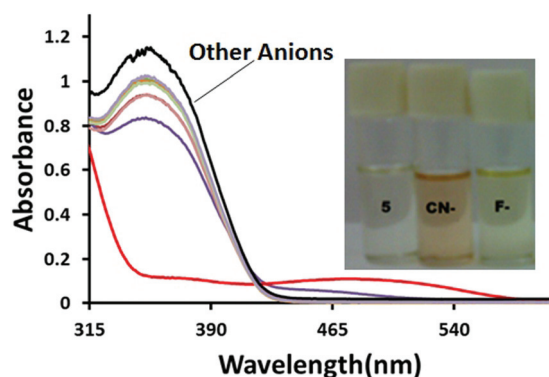

Fig. 6 Changes in the UV-vis spectrum of (**5**) in DMSO (10 μM) on the addition of various anions (100 μM).
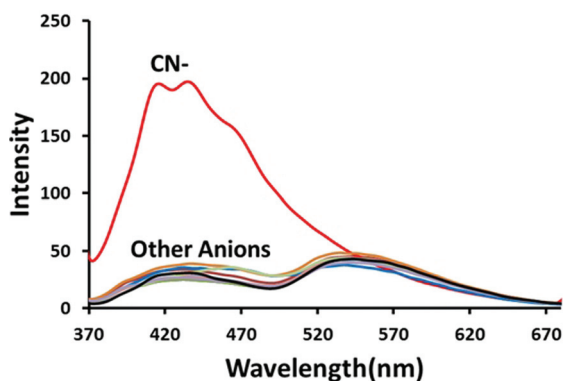

Fig. 7 Changes in fluorescence intensity of (**5**) in DMSO (10 μM) on the addition of various anions (100 μM).

higher concentration of CN⁻ ion or after a longer reaction time than (**4**). Due to this slow chemodosimeter response (**5**) can be used as a very selective and sensitive chromo/fluorogenic sensor for CN⁻ ion exclusively, transducing different naked eye

chromo/fluorogenic responses at low and high concentrations of the anion.

The fluorescence spectra of (**5**) exhibited emission bands at $\lambda_{(ems)}$ 437 nm and $\lambda_{(ems)}$ 545 nm. The intensity of the former band enhances up to ten fold on addition of TBACN (Fig. S27a†) but not with other anions (Fig. S27b†). This gives a blue color fluorescence (Fig. S22b†) at very high anion concentration or after 24 hours. This effect may be due to a PET phenomenon which is reduced when –OH is involved in H-bonding with the anion resulting in enhancement of signal.

¹H NMR titration experiments of (**5**)

The ¹H NMR and mass spectra (Fig. S28†) of the sensor with 20 and 30 equivalents of CN⁻ ion again shows (Fig. 8) the absence of OH and imine signals, up field shift of aromatic protons, appearance of the –NH signal at δ 5.69 ppm.

Colorimetric response of sensors in semi-aqueous medium

Since the chemodosimetric detection of CN⁻ ion is irreversible in water the efficacy of (**4**) and (**5**) was checked in water by using aqueous solutions of (100 μM) TBACN, NaCN and NaSCN in a DMSO solution of (**4**) and (**5**) (10 μM, DMSO : water 2 : 1) which resulted in a similar response as in DMSO in the form of appearance of red color (Fig. 9) in the solution.

In order to confirm this proposed mechanism (Scheme 2), the nitrile product from **4** and NaCN was synthesized, separated, purified and analyzed by ¹H NMR, IR and mass spectrometry (Fig. S29–S31†). Apparently any hydrolysis of the nitrile into amino acid has not occurred because of the absence of any acid in the reaction medium at this stage.

Conclusions

In summary, we have developed two new –OH containing Schiff base receptors as F⁻ and CN⁻ ion sensors. Catechol based sensor (**4**) works for both F⁻ and CN⁻ ions, albeit through different channels in DMSO. Its colorimetric response
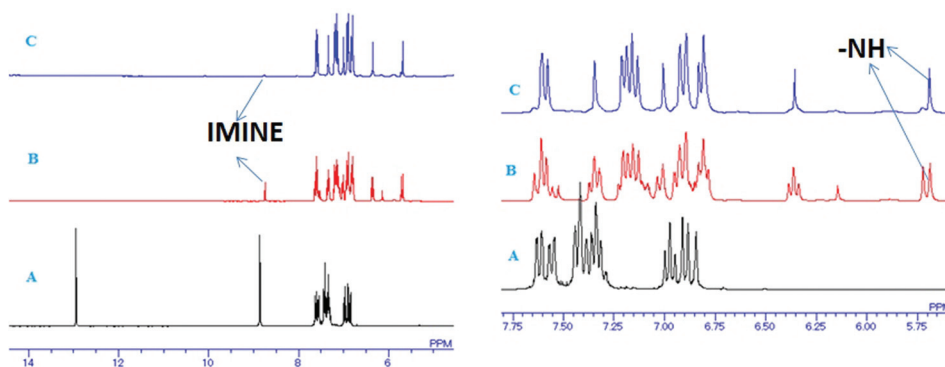
658 | *Org. Biomol. Chem.*, 2013, **11**, 654–661

This journal is © The Royal Society of Chemistry 2013

Fig. 8 Showing partial ^1H NMR of (5 mM) solution of (**5**) in DMSO-d_6 with (A) no TBACN (B) 20 equivalent TBACN (C) 30 equivalent TBACN.
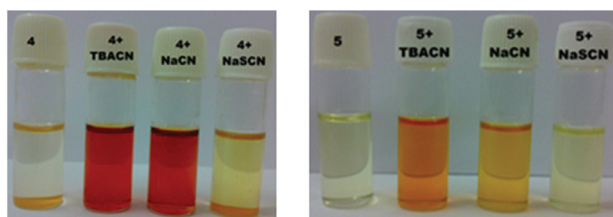

Fig. 9 Showing colorimetric response of **4** and **5** with TBACN, NaCN and NaSCN in DMSO : water 2 : 1 solution.

may be used to discriminate between the two anions within two minutes whereas its fluorogenic response may do so instantaneously and with high sensitivity. In DMSO : water (**4**) behaves as a colorimetric sensor exclusively for CN⁻ ion. The phenol based sensor (**5**) is a highly selective one for CN⁻ ion and may be used as a semiquantitative chromo/fluorogenic sensor sensing CN⁻ with colorimetric and fluorogenic responses for different CN⁻ ion concentrations. The chemo-dosimeter response of these sensors towards CN⁻ ion is due to a Strecker's nucleophilic addition to imine bond of the Schiff bases.

Experimental

General information

All the commercially available chemicals were purchased from Aldrich and used without further purification. All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. TLC was carried out on glass sheets pre-coated with silica gel. The ^1H and ^{13}C NMR spectra were carried out in DMSO-d_6 with TMS as an internal reference, on a 300 MHz NMR spectrophotometer. The infra-red spectra (KBr pellet) were recorded using a Varian IR spectrophotometer in the range 400–4000 cm^{-1}. The electronic absorption spectra were recorded on a Shimadzu Phramaspec UV-1700 UV-vis spectrophotometer. Mass spectra were recorded on a Bruker's microTOF-QII spectrophotometer.

Compounds **2** and **3** were commercially available. The dipodal amine was prepared as already reported by us.[12]

X-ray measurement and structure determination

The crystals of compound (**5**) were grown by slow evaporation from mixture of CHCl$_3$ and CCl$_4$. X-ray data of the compound (**5**) was collected on a Bruker's Apex-II CCD diffractometer using Mo Kα (λ = 0.71069) at room temperature. The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. A total of 19 836 reflections were measured out of which 5877 were independent and 3146 were observed [$I > 2\sigma(I)$] for theta 25°. The structure was solved by direct methods in a trigonal $R\bar{3}$ space group, using SIR-92 and refined by full-matrix least squares refinement methods based on F^2, using SHELX-97. The refinement showed a disordered CCl$_4$ molecule in the structure with C and one Cl atom lying on the three fold axis with site occupancy of 0.3333. The disorder in other Cl atom was resolved by splitting it in two positions and refining anisotropically with restraints on C–Cl bonding and Cl···Cl non-bonding distances. The hydrogens of the –OH groups were located from the difference Fourier synthesis and were refined isotropically with U_{iso} values 1.2 times that of their carrier oxygen atoms, with restraints on the O–H distance. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbons. All calculations were performed using Wingx package.

UV-vis and fluorescence studies

Molecular interaction of **4** and **5** with all anions under study were investigated using UV–vis spectroscopy at 10^{-5} M and fluorescence spectroscopy at 5 × 10^{-6} M for **4** and 10^{-5} M for **5** in DMSO solution. The changes in the UV-vis spectra of sensors on the gradual addition of TBAF and TBACN were recorded at a concentration of 10^{-4} M while for fluorescence the concentration of anions used for **4** was 5 × 10^{-5} M and 10^{-4} M for **5**.

This journal is © The Royal Society of Chemistry 2013

Org. Biomol. Chem., 2013, **11**, 654–661 | **659**

Job's plot and stability constant determination

The binding stoichiometry of sensor–anion complexes was determined by the method of continuous variation (Job's plot). Ten solutions were made by varying L : M ratio and keeping the total concentration of **4** and **5** and anionic guest constant (5×10^{-5} M) with continuous variation of the mole fraction of **4** and **5**. The results indicate the formation of complexes with stoichiometric ratio of 1 : 1 for TBAF in case of **4** and 1 : 2 for TBACN in case of **4** and **5**. The stability constant of these complexes were determined by a Benesi–Hildebrand plot.

Synthesis of compounds

Compound (4). Compound **1** (0.20 g, 0.510 mmol) was dissolved in 10 ml chloroform, to which was added 0.15 g (1.08 mmol) of 2,3-dihydroxybenzaldehyde in 40 ml of methanol along with 3–4 mg of zinc perchlorate. The color of the solution changed immediately to dark orange from light yellow and a precipitate separated out within half an hour. The precipitate was filtered, washed with methanol and dried. Yield 76%. Orange solid; mp = 165–167 °C; IR (KBr, cm^{-1}) 1612, 3382 (br); ^{1}H NMR (300 MHz, DMSO-d$_6$, δ): 2.23 (s, 6H, –CH$_3$), 2.38 (s, 3H, –CH$_3$), 4.12 (s, 4H, –CH$_2$), 6.79 (t, 2H, –Ar, J = 7.8), 6.88 (s, 1H, –Ar), 6.92 (d, 2H, –Ar, J = 9.0), 7.07 (d, 2H, –Ar, J = 7.95), 7.28–7.39 (m, 4H, –Ar), 7.48 (d, 2H, J = 7.65), 7.56 (d, 2H, J = 7.5), 8.87 (s, 2H, –CH=N), 9.08 (s, 2H, –OH), 13.05 (s, 2H, –OH); ^{13}C NMR (75 MHz, DMSO-d$_6$, δ): 14.9 (–CH$_3$), 19.2 (–CH$_3$), 31.6 (–CH$_2$), 117.8 (–Ar), 118.9 (–Ar), 119.2 (–Ar), 122.9 (–Ar), 126.1(–Ar), 127.1(–Ar), 127.8 (–Ar), 130.3 (–Ar), 133.5 (–Ar), 136.4 (–Ar), 144.9 (–Ar), 145.5 (–Ar), 148.9 (–Ar), 162.9 (CH=N); Elemental analysis calculated for C$_{37}$H$_{34}$N$_2$O$_4$S$_2$: C, 70.00; H, 5.40; N, 4.41; S, 10.10%. Found: C, 69.99; H, 5.31; N, 4.30; S, 10.08%; HRMS m/z 657.21 [M + Na] ion.

Compound (5). Compound **1** (0.20 g, 0.331 mmol) was dissolved in 10 ml chloroform, to which was added 0.0810 g (0.663 mmol) of 2-hydroxybenzaldehyde in 40 ml of methanol along with 3–4 mg of zinc perchlorate. The reaction mixture was stirred for 2 h, after the completion of the reaction the solvent was evaporated and the product was recrystallized from methanol as a yellow solid. Yield 60%. mp = 110–112 °C; IR (KBr, cm^{-1}) 1608, 3411; ^{1}H NMR (300 MHz, DMSO-d$_6$, δ): 2.23 (s, 6H, –CH$_3$), 2.30 (s, 3H, –CH$_3$), 4.09 (s, 4H, –CH$_2$), 6.82 (s, 1H, –Ar), 6.88 (d, 2H, –Ar, J = 8.1), 6.95 (t, 2H, –Ar, J = 7.5), 7.32 (t, 4H, –Ar, J = 6.3), 7.40 (t, 4H, –Ar, J = 8.1), 7.54 (d, 2H, J = 6.3), 7.60 (d, 2H, J = 6.9), 8.84 (s, 2H, –CH=N), 12.92 (s, 2H, –OH); ^{13}C NMR (75 MHz, DMSO-d$_6$, δ): 14.8 (–CH$_3$), 19.2 (–CH$_3$), 31.7 (–CH$_2$), 116.6 (–Ar), 118.0 (–Ar), 126.4 (–Ar), 127.6 (–Ar), 129.9 (–Ar), 130.3 (–Ar), 132.7 (–Ar), 133.1 (–Ar), 133.4 (–Ar), 136.3 (–Ar), 136.7 (–Ar), 145.7 (–Ar), 160.2 (–Ar), 162.7 (CH=N); Elemental analysis calculated for C$_{37}$H$_{34}$N$_2$O$_2$S$_2$: C, 73.72; H, 5.69; N, 4.65; S, 10.64%. Found: C, 73.73; H, 5.54; N, 4.62; S, 10.59%; HRMS m/z 603.21 [M + 1]$^+$ ion.

Compound (6). Compound **4** (0.20 g, 0.292 mmol) was dissolved in 5 ml DMSO, to which was added 0.143 g (2.918 mmol) of NaCN. The reaction mixture was stirred for

5 h, the color of the solution changed from light yellow to dark red. Dry chloroform (20 ml) was added to the reaction mixture and then it was stirred for five minutes. A dark reddish brown precipitate separated out, was separated by filtration and washed with chloroform. Then the compound was dried under vacuum. Yield 40%. mp = above 300 °C; IR (KBr, cm^{-1}) 2246; ^{1}H NMR (300 MHz, DMSO-d$_6$, δ): 2.23 (s, 2H, –NH), 2.32 (s, 6H, –CH$_3$), 2.54 (s, 3H, –CH$_3$), 3.97 (s, 4H, –CH$_2$), 4.04 (s, 2H, –CH), 6.50–7.88 (m, 15H, –Ar); Elemental analysis calculated for C$_{39}$H$_{32}$N$_4$O$_4$S$_2$: C, 68.40; H, 4.71; N, 8.18; S, 9.36%. Found: C, 68.48; H, 4.65; N, 8.08; S, 9.25%.

References

1 (a) J. L. Sessler, P. A. Gale and W. S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, UK, 2006; (b) P. A. Gale and R. Quesada, *Coord. Chem. Rev.*, 2006, **250**, 3219; (c) T. Gunnlaugsson, M. Glynn, G. M. Tocci (nee Hussey), P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094; (d) J. W. Steed, *Chem. Commun.*, 2006, 2637; (e) M. H. Filby and J. W. Steed, *Coord. Chem. Rev.*, 2006, **250**, 3200; (f) B. T. Nguyen and E. V. Anslyn, *Coord. Chem. Rev.*, 2006, **250**, 3118; (g) J. L. Sessler and J. M. Davis, *Acc. Chem. Res.*, 2001, **34**, 989; (h) F. Sancenòn, A. B. Descalzo, R. Martinez-Máñez, M. A. Miranda and J. Soto, *Angew. Chem., Int. Ed.*, 2001, **40**, 2640; (i) D. H. Lee, H. Y. Lee and J.-Ju. Hong, *Tetrahedron Lett.*, 2002, **43**, 7273.

2 (a) J. Yoon, S. K. Kim, N. J. Singh and K. S. Kim, *Chem. Soc. Rev.*, 2006, **35**, 355; (b) V. Amendola, M. Vonizzoni, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, F. Sancenòn and A. Taglietti, *Coord. Chem. Rev.*, 2006, **250**, 1451; (c) R. Martinez-Máñez and F. Sancenòn, *J. Fluoresc.*, 2005, **15**, 267; (d) R. Martinez-Máñez and F. Sancenòn, *Chem. Rev.*, 2003, **103**, 4419; (e) P. A. Gale, *Acc. Chem. Res.*, 2006, **39**, 465; (f) F. P. Schmidtchen, *Coord. Chem. Rev.*, 2006, **250**, 2918.

3 (a) K. L. Krik, *Biochemistry of Halogens and Inorganic Halides*, Plenum Press, New York, 1991, 591; (b) M. Kleerekoper, *Endocrinol. Metab. Clin. North Am.*, 1998, **27**, 441; (c) S. Matsuo, K. Kiyomiya and M. Kurebe, *Arch. Toxicol.*, 1998, **72**, 798; (d) D. Briancon, *Rev. Rhum. Engl. Ed.*, 1997, **64**, 78; (e) K. J. Wallace, R. I. Fagmemi, F. J. Folmer-Anderson, J. Morey, V. M. Lynth and E. V. Anslyn, *Chem. Commun.*, 2006, 3886; (f) T. J. Dale and J. Rebek, *J. Am. Chem. Soc.*, 2006, **128**, 4500.

4 (a) K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281; (b) C. Serre, F. Millange,

C. Touvenot, M. Nogués, G. Marsolier, D. Louër and G. férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519; (*c*) A. A. Baykov, I. P. Fabrichniy, P. Pohjanjoki, A. B. Zyryanov and R. Lahti, *Biochemistry*, 2000, **39**, 11939.

5 C. Young, L. Tidwell and C. Anderson, *Cyanide: Social, Industrial and Economic Aspects: Minerals, Metals and Materials Society*, Warrendale, 2001.

6 *Guidelines for drinking water quality*, World Health Organization, Genava, 1996.

7 (*a*) R. Badugu, J. R. Lakowicz and C. D. Geddes, *J. Am. Chem. Soc.*, 2005, **127**, 3635; (*b*) S.-S. Sun, A. J. Lees and P. Y. Zavalij, *Inorg.Chem.*, 2003, **42**, 3445; (*c*) P. Anzenbacher Jr., D. S. Tyson, K. Jursikova and F. N. Castellano, *J. Am. Chem. Soc.*, 2002, **124**, 6232; (*d*) H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2001, **40**, 154.

8 R. Martinez-Mánez and F. Sancenòn, *Coord. Chem. Rev.*, 2006, **250**, 3081.

9 J. Isaad and A. E. Achari, *Tetrahedron*, 2011, **67**, 5678.

10 (*a*) Y. Sun, Y. Liu, M. Chen and W. Guo, *Talanta*, 2009, **80**, 996; (*b*) Y. Sun, Y. Liu and W. Guo, *Sens. Actuators, B*, 2009, **143**, 171.

11 (*a*) K. Surendra, N. S. Krishnaveni, A. Mahesh and K. R. Rao, *J. Org. Chem.*, 2006, **71**, 2532; (*b*) B. A. B. Prasad, A. Bisai and V. K. Singh, *Tetrahedron Lett.*, 2004, **45**, 9565.

12 V. K. Bhardwaj, S. Sharma, N. Singh, M. S. Hundal and G. Hundal, *Supramol. Chem.*, 2011, **23**, 790.

13 (*a*) W.-K. Lo, W.-K. Wong, J.-P. Guo, W.-Y. Wong, K.-F. Li and K.-W. Cheah, *Inorg. Chim. Acta*, 2004, **357**, 4510; (*b*) P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 2000, **122**, 10405; (*c*) A. Filarowski, A. Koll and T. Glowiak, *J. Chem. Soc., Perkin Trans. 2*, 2002, 835; (*d*) V. K. Bhardwaj, A. P. S. Pannu, N. Singh, M. S. Hundal and G. Hundal, *Tetrahedron*, 2008, **64**, 5384.

14 (*a*) N. Singh, M. Kumar and G. Hundal, *Inorg. Chim. Acta*, 2004, **14**, 4286; (*b*) D. Luneau and C. Evans, *J. Chem. Soc., Dalton Trans.*, 2002, 83.

15 G.-J. Kim and H.-J. Kim, *Tetrahedron Lett.*, 2010, **51**, 2914.

16 (*a*) R. Yanada, M. Okaniwa, A. Kaieda, T. Ibuka and Y. Takemoto, *J. Org. Chem.*, 2001, **66**, 1283; (*b*) Y. Yamamoto, K. Maruyama, T. Komatsu and W. Ito, *J. Am. Chem. Soc.*, 1986, **108**, 7778.

17 W. Rodriguez-Cordoba, J. S. Zugazagoitia, E. Collado-Fregoso and J. Peon, *J. Phys. Chem. A*, 2007, **111**, 6241.